

CONWY

SCIENCE TUTOR



WJEC A LEVEL

ALIPHATIC

OXYGEN

CONTAINING

COMPOUNDS

QUESTIONS 2

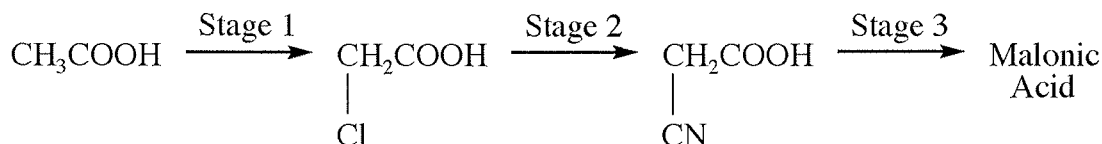
WITH ANSWERS

SECTION B

Answer **both** questions in the separate answer book provided.

4.1 Malonic acid, $C_3H_4O_4$, can be formed from several naturally-occurring chemicals.

- (a) (i) Giving reagent(s) and expected observation(s), outline one test which could be used to show that malonic acid is a carboxylic acid. [2]
- (ii) 1.04 g malonic acid needed 16.0 cm^3 sodium hydroxide of concentration 1.25 mol dm^{-3} for complete reaction. Calculate the number of moles of sodium hydroxide which react with one mole of malonic acid. [2]
- (iii) The proton NMR spectrum of malonic acid showed only two peaks, at 3.2 ppm and 11.5 ppm. The two peaks were both singlets (no splitting present) and of equal area.
Using **all** the information given in (a), and showing your reasoning, draw the structure of malonic acid. [4]
- (iv) State the systematic name for malonic acid. [1]
- (b) Malonic acid was originally synthesized from ethanoic acid by the following reaction sequence.



State the reagent(s) and condition(s) necessary to carry out stage 1 and stage 2. [4]

- (c) Decarboxylation of malonic acid gives a mixture of two organic products.
- (i) State the reagent used for the decarboxylation of carboxylic acids. [1]
- (ii) Name the two organic products possible from the decarboxylation of malonic acid. [2]
- (d) Malonic acid is also formed by the oxidation of malonaldehyde, a suspected carcinogenic initiator and mutagen produced during the cooking of meats. One step in the test for malonaldehyde in food involves reacting it with 2,4-dinitrophenylhydrazine (2,4-DNPH) to form an orange solid. For this reaction:
- state the group for which reaction with 2,4-DNPH is a test;
 - classify the type of reaction occurring;
 - outline how the orange solid can be separated and used to identify the original compound being tested. [4]

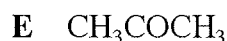
Total [20]

Section B

- 1 (a) (i) Add malonic acid to (saturated) sodium hydrogencarbonate / sodium carbonate solution. (1)
 Effervescence / bubbling / fizzing occurs (*not* "gas produced"). (½)
 Gas turns limewater milky / cloudy (½) [2]
- (ii) M_r malonic acid = 104.04 (allow 104) (1)
 moles malonic acid = $1.04 / 104.04 = 0.0100$ (1)
- $$\text{moles NaOH} = \frac{1.25 \times 16.0}{1000} = 0.0200$$
- ∴ 2 mol NaOH per 1 mol acid. (1)
- 2 marks for 2:1 ratio with no working
 Mark consequentially if incorrect. [2]
- (iii) 3.2 ppm shows -CH₂CO- group
 11.5 ppm shows -COOH group $2 \times (½)$
- Singlets, so no Hs on adjacent atoms (1)
- 2 COOH groups per molecule (since 2 NaOH needed) (1)
- Only possible structure is HOOC-CH₂-COOH (1) [4]
- (iv) Propanedioic acid or 1,3 Propanedioic acid (1) [1]
 (Mark consequentially if incorrect structure given).
- (b) Stage 1 Chlorine gas / Cl₂ (1)
 room temperature and UV / daylight $2 \times (½)$
- Stage 2 KCN or Na CN or CN⁻ (1)
 ethanol (aqueous) / other suitable solvent (½)
 room temperature / gentle warming (½) [4]
- (c) (i) Sodalime. [1]
- (ii) Ethanoic acid / sodium ethanoate (loss of one CO₂)
 Methane (loss of two CO₂) $2 \times (1)$ [2]
- (d) Carbonyl group / aldehyde or ketone (both needed) (1)
 Condensation *or* addition- elimination reaction (1)
 Orange (hydrazone) solid is (filtered off and) purified (1)
 Melting temperature determined (to identify original carbonyl compound) (1) [4]

Total [20]

2 (a) Consider the following six compounds:



- (i) State, giving an explanation, which compound would have the highest boiling temperature. [2]
- (ii) Describe a reaction where compounds **D** and **E** show a similar chemical reaction. [1]
- (iii) For **each** of the following pairs of compounds, describe a **chemical** test that can be used to distinguish between them. The reagent(s) as well as the observation(s) for **each** compound, are required.
- I. Compounds **D** and **E** [2]
- II. Compounds **B** and **C** [2]
- (iv) State the reagent(s) and condition(s) needed for each stage in the following synthesis.



- (b) Although ethylamine can be prepared directly from chloroethane, phenylamine cannot be prepared directly from chlorobenzene. However, phenylamine can be synthesised from benzene.
- (i) State the type of reaction taking place when chloroethane is converted into ethylamine. [1]
- (ii) Give a reason why phenylamine cannot be prepared directly from chlorobenzene. [1]
- (iii) Outline a **two** step synthesis of phenylamine from benzene. Your answer should include reagents and conditions for **each** step. [4]
- (c) During a synthesis of phenylamine from benzene, 10.0 cm^3 of benzene produced 4.20 cm^3 of phenylamine. Given that the density of benzene is 0.878 g cm^{-3} , and that of phenylamine is 1.00 g cm^{-3} , calculate the percentage yield of the synthesis correct to 3 significant figures. [3]

Total [20]

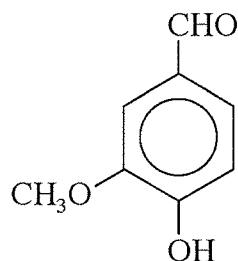
Section B Total [40]

- 5/2 (a) (i) $\text{CH}_3\text{CH}_2\text{COOH}$ (1)
 Contains strongest hydrogen bonding between molecules (1)
 (accept can form hydrogen bond in 2 places) [2]
- (ii) Reduction with NaBH_4 to give alcohol / Reaction with 2,4-DNP to give orange precipitate / Addition of HCN to give hydroxynitrile [1]
- (iii) I. Tollens' Reagent (ammoniacal silver nitrate) / Fehling's solution (1)
 $\text{CH}_3\text{CH}_2\text{CHO}$ gives silver mirror / red ppt, CH_3COCH_3 no reaction (1) [2]
 (accept iodoform reaction / oxidation)
- II. Add alkaline iodine solution / KI and NaOCl solution (1)
 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ gives yellow precipitate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ no reaction (1) [2]
- (iv) $\text{Na}_2\text{Cr}_2\text{O}_7 / \text{KMnO}_4$ (Accept $\text{Cr}_2\text{O}_7^{2-} / \text{MnO}_4^-$) (1)
 Acidified and reflux (heat) (1)
 (conditions mark can be given if formula incorrect)
 CH_3OH (1)
 Concentrated H_2SO_4 and warm (1)
 (conditions mark can be given if wrong alcohol given) [4]
- (b) (i) Nucleophilic substitution [1]
- (ii) C-Cl bond difficult to break due to interaction of Cl p orbitals with delocalised π electrons in benzene [1]
- (iii) Concentrated nitric acid and sulphuric acid (1)
 At 50 – 60 °C to give nitrobenzene (1)
 Concentrated hydrochloric acid, tin (1)
 and heat followed by sodium hydroxide (1) [4]
- (c) Mass benzene used = $0.878 \times 10 = 8.78 \text{ g}$
 Moles benzene = $\frac{8.78}{78.06} = 0.112$ (1)
 Moles phenylamine = $\frac{4.20}{93.70} = 0.0451$ (1)
 $\% \text{ yield} = \frac{0.0451}{0.112} \times 100 = 40.3\%$ (1) [3]

Total [20]

Total Section B [40]

3. (a) Vanillin, shown below, is used as flavouring in food. It can be detected by most individuals at a level of 0.1 parts per million.



In the questions which follow, the methoxy ($\text{CH}_3\text{O}-$) group can be assumed to be unreactive.

- (i) Describe **one** test to show the presence of each of the groups $-\text{CHO}$ and $-\text{OH}$ in vanillin by giving the reagent(s) and expected observations.

$-\text{CHO}$ test:

Reagents

.....

Observations

.....

$-\text{OH}$ test:

Reagents

.....

Observations

.....

[4]

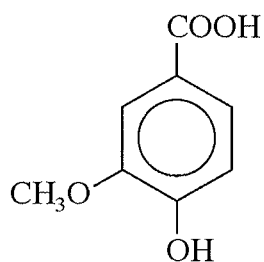
- (ii) I. Draw the structure of the compound formed by the addition of hydrogen cyanide, HCN , to the $-\text{CHO}$ group in vanillin.

[1]

- II. Draw the mechanism by which this addition reaction occurs in the space below. You may represent vanillin as R-CHO in this mechanism.

[3]

- (b) Oxidation of vanillin produces vanillic acid, shown below, which can be detected in wood smoke and cooked food.



The methoxy (CH₃O-) group can again be assumed to be unreactive.

- (i) Explain why, when vanillic acid dissolves in dilute aqueous sodium hydroxide, one mole of vanillic acid reacts with two moles of alkali.

.....

.....

[1]

- (ii) Vanillic acid can form an ester on reaction with ethanol.

- I. State the conditions necessary for the esterification to occur.

.....

.....

[1]

- II. Draw the structure of the ester produced.

[1]

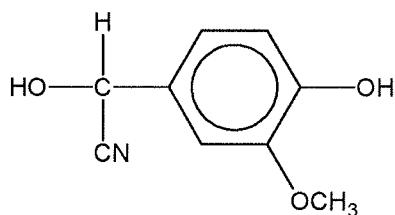
Total [11]
Section A Total [35]

Turn over.

- Q.3 (a) (i)** -CHO test Tollens reagent/ammoniacal silver nitrate. (1)
Silver mirror on warming. (1)
- or
- Fehling's solution/alkaline Cu(II) complex. (1)
(Red-)brown precipitate on heating. (1)
- OH test (Neutral) iron(III) chloride / FeCl₃. (1)
Produces purple colour. (1)
- or
- Bromine (in aqueous KBr). (1)
Produces white precipitate. (1)

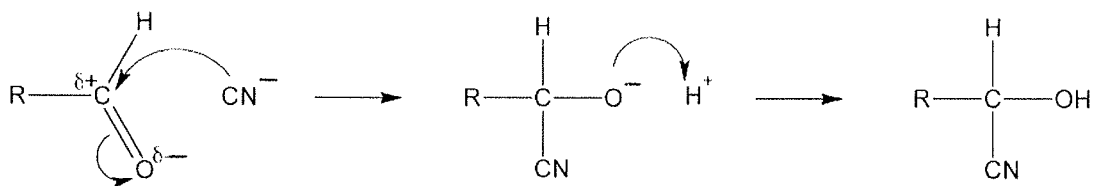
[4]

(ii) I



(1)

II



(1/2) dipoles
2 × (1/2) electron movements
(1/2) CN⁻ (as nucleophile).

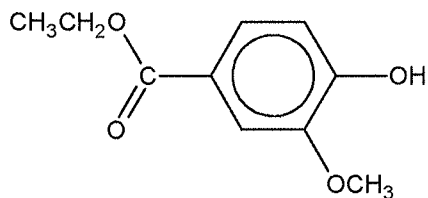
(1/2) structure
(1/2) movement

[3]

(b) (i) Both phenol and carboxylic group are acidic and react with alkali. (1)[1]

(ii) I Reflux/heat (1/2) with conc sulphuric acid (catalyst) (1/2). [1]

II



(1)

[1]

Total = [11]